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European Patent Office  
Office européen des brevets

(11) Publication number:

**0 257 193  
A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 87106482.0

(51) Int. Cl.4: H05K 1/09

(22) Date of filing: 05.05.87

(30) Priority: 27.08.86 JP 200731/86

(43) Date of publication of application:  
02.03.88 Bulletin 88/09

(64) Designated Contracting States:  
DE FR GB IT NL

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(54) Low-temperature burnt conductive paste and method of manufacturing printed circuit board.

(57) Disclosed are a low-temperature burnt conductive paste which is prepared in such a manner that a base material consisting of 50 to 95% by weight of a powder of at least one conductive material selected from the group consisting of copper, a copper alloy containing copper as a major component, and oxides thereof and 5 to 50% by weight of a glass powder having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $6$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  is dispersed in an organic vehicle, and a method of manufacturing a printed circuit board using the paste.

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Low-temperature burnt conductive paste and method of manufacturing printed circuit board

The present invention relates to a burnt conductive paste used for a printed circuit board for an internal wiring material of electronic equipment and the like and a method of manufacturing a printed circuit board using the same.

A conventional conductive paste of this type consists of a metal powder, a glass frit, and an organic vehicle. As the metal powder, metals such as Au, Ag, Ag-Pd, Cu, and the like are used. These conductive pastes are printed on insulating boards and burnt at a temperature of about 900°C to form thick films. The resultant structures are used as conductor circuits having a specific resistance of about  $5 \times 10^{-5} \Omega \cdot \text{cm}$  or less.

As the insulating boards used for these conductive pastes, ceramic boards, in particular, alumina boards, which do not change at the burning temperature, which have a sufficient adhesive strength with the conductive pastes, and which have good electrical insulating properties, are used.

Since Au, Ag, and Pd are expensive, Cu paste has recently received a great deal of attention. Copper (Cu) is inexpensive and has good characteristics, in that it has a good electrical conductivity and soldering properties, and it does not easily cause migration, and so on.

However, since copper is easily oxidized, it cannot be burnt in air, and must be burnt in a nitrogen atmosphere having a specific oxygen partial pressure in which an organic vehicle can be evaporated and copper is not oxidized, resulting in cumbersome operations. For this reason, a current Cu paste is expensive.

Recently, a conductive paste using copper oxide has been proposed. In this paste, a small amount of a Pt powder, a Pd powder, an Ni powder, or a manganese oxide powder is added to a copper oxide powder, the resultant mixture is burnt at a temperature of about 700°C in air and is then reduced in a reducing atmosphere at a temperature of about 1,000°C, thereby preparing a conductor. In this method, strict atmospheric control is not necessary. However, burning at this temperature aims at the same applications and effects as those of the Cu paste, and the resultant paste is assumed to be applied to a ceramic board such as an alumina board, as the board material. However, since the conductive pastes use expensive noble metals, they are still expensive (Japanese Patent Disclosure (Kokai) Nos. 61-289691, 61-292394, and 61-292393).

Recently, another conductive paste which can be burnt at a temperature of about 500 to 675°C has been proposed. The conductive paste consists of a metal powder such as a powder of Ag, Cu, Ag alloy, Cu alloy, or the like, a glass frit, and an organic vehicle. The mixture is burnt while an amount of the glass frit is increased in order to improve the adhesive strength to the board and the mechanical strength of the resultant thick film (Japanese Patent Disclosure (Kokai) Nos. 58-71507 and 58-10302).

In addition, still another conductive paste containing a copper oxide powder as a base material is proposed. In this paste, 7 to 27% by weight of boron, 0 to 35% by weight of a glass frit, and the balance of the copper oxide powder are dissolved in the organic vehicle, and the resultant paste is heated in air at a temperature of 500 to 675°C to prepare a thick film conductor (Japanese Patent Disclosure (Kokai) No. 57-55005).

However, the resultant conductive film obtained by heating the conductive paste in air has an unsatisfactory conductivity of  $10 \Omega/\square$  or lower and poor soldering properties. Therefore, this paste cannot be used for a printed circuit board.

As described above, since the conventional copper oxide based conductive pastes aim at only decreasing a burning temperature of the paste in view of energy cost, the pastes having a low conductivity can only be obtained.

In consideration of the above situation, the present inventors have made extensive studies, and as a result, developed a conductive paste which can be burnt at a low temperature of 300 to 600°C, and with which a resultant conductor circuit can have a sufficient adhesive strength with an insulating board and a circuit having a high conductivity and good soldering properties can be formed.

More specifically, the present invention relates to a low-temperature burnt conductive paste prepared by dispersing, in an organic vehicle, a base material comprising 50 to 95% by weight of a powder of at least one conductive material selected from the group consisting of copper, a copper alloy containing copper as a major component, and oxides thereof, and 5 to 50% by weight of a glass powder having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $6$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ , and to a method of manufacturing a printed circuit board comprising forming a circuit pattern on an insulating inorganic board by a desired process using the conductive paste, heating the resultant structure in air at a temperature of 300 to 600°C, and then heating the structure in a reducing atmosphere at a temperature of 400 to 600°C.

A conventional copper based conductive paste is burnt in a non-oxidizing atmosphere so as not to oxidize copper. However, in contrast to this, a conductive paste of the present invention can be burnt at low temperatures by oxidizing copper.

In general, since an oxide film is provided on the surface of a metal powder particle, a burning temperature cannot be decreased. For this reason, a burning process is normally performed in a reducing atmosphere. However, if an organic vehicle is contained like in a conductive paste, the burning process cannot be performed in the reducing atmosphere to evaporate the organic vehicle.

In the conductive paste of the present invention, the first burning process is performed in air to evaporate the organic vehicle and to improve wetting properties between the copper oxide and glass, thereby improving the mechanical strength of a resultant conductive film. During the second burning process in the reducing atmosphere, copper oxide is reduced and at the same time, sintering is accelerated, that is, activated sintering is performed, thereby forming a conductive film having a good electrical conductivity. In the conductive paste of the present invention, a copper powder, a copper alloy powder, and an oxide powder thereof are not sufficient to allow the burning process at a low temperature, and they are combined with glass having a low softening point, thereby obtaining a conductive paste having satisfactory characteristics.

Since the conductive paste of the present invention aims at burning at a low temperature, if it is burnt at a high temperature, satisfactory characteristics cannot be obtained. More specifically, if the burning process is performed in air at a temperature of 650°C or higher,  $\text{Cu}_2\text{O}$  reacts with an oxide such as  $\text{PbO}$  as a component of glass, and a composite oxide is formed. As a result, desired copper cannot be obtained in the burning process in the reducing atmosphere.

Particles of copper alloy, copper, and/or an oxide thereof are flattened to increase the specific surface area of the particles, to increase the area of contact with the board, and to increase the area of contact with a glass phase. Therefore, a high adhesive strength can be obtained. When the specific surface area is large, a probability of contact of powder particles is increased, and a conductivity can also be improved.

If an oxide powder of a copper alloy containing silver, tin, and the like is used, soldering properties can be improved.

In the conductive paste of the present invention, the reason why a content of a glass powder having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $6$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  is limited to 5 to 50% by weight is as follows. If the content is lower than 5% by weight, the resultant paste is poor in adhesion to the insulating board. If the content exceeds 50% by weight, soldering properties to a circuit board prepared by using the paste of the present invention are considerably degraded.

Low softening-point glasses having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $6$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  include  $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$  based glass,  $\text{ZnO-B}_2\text{O}_3\text{-PbO}$  based glass, and the like. A small amount of an oxide such as  $\text{BaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ , or the like can be contained in these glasses. A glass powder preferably has a size smaller than 325 mesh.

A conductive material powder preferably has a particle size of 10  $\mu\text{m}$  or smaller, and a flattening ratio of 1.5 or higher in terms of the conductivity of the resultant paste and an adhesive strength to the insulating board.

When an oxide of copper or a copper alloy is used as a conductive material, one having an oxidation ratio of 0.1 to 100% is preferable. The oxidation ratio represents an oxygen content in percentage by weight when  $\text{Cu}_2\text{O}$  is 100% and  $\text{Cu}$  is 0%. As a copper alloy containing copper as a major component, one selected from the group consisting of  $\text{Cu-Ag}$ ,  $\text{Cu-Sn}$ , and  $\text{Cu-Ag-Sn}$ , and having an  $\text{Ag}$  content of 0.05 to 50% by weight and an  $\text{Sn}$  content of 0.01 to 10% by weight, is preferable.

As an organic vehicle, one prepared by dissolving about 10% by weight of a material such as ethyl cellulose, saturated fatty acid-modified alkyd resin, or the like in butyl carbitol or turpentine oil can be used. A mixing ratio of the base material and the organic vehicle can be determined in association with a viscosity of the resultant paste.

The conductive paste of the present invention is printed on a ceramic board, a porcelain enamel board, or the like by screen printing. After drying, the board is heated in air at a temperature of 300 to 600°C, and thereafter, is heated in the reducing atmosphere at a temperature of 400 to 600°C, thereby preparing a conductor circuit.

The present invention will be described hereinafter by the way of its examples.

## Example 1

A copper oxide powder having an average particle size of  $0.6 \mu\text{m}$  and a  $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$  based glass powder having a softening point of about  $400^\circ\text{C}$  and a coefficient of thermal expansion  $8.5 \times 10^{-6}^\circ\text{C}^{-1}$  (glass composition: 4.5% of  $\text{SiO}_2$ , 70% of  $\text{PbO}$ , 15.5% of  $\text{B}_2\text{O}_3$ , 8% of  $\text{ZnO}$ , and 2% of  $\text{Al}_2\text{O}_3$ ) were mixed at various mixing ratios to prepare base materials. These base materials were dispersed in an organic vehicle prepared such that 10% by weight of ethyl cellulose was dissolved in butyl carbitol, thereby preparing conductive pastes. The conductive pastes were screen-printed on alumina boards, and were respectively burnt at temperatures shown in Table 1. The specific resistance, the adhesive strength, and the soldering properties of the resultant conductors were tested. The test results are shown in Table 1.

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Table 1

No.	Glass Content (wt.%)	Copper Oxide Content (wt.%)	Oxidation Ratio (%)	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength ( $\text{kg/mm}^2$ )	Soldering Property	Total Evaluation
				In Air	In Hydrogen Atmosphere				
1	0	100	90	500	500	$1 \times 10^{-3}$	0	$\Delta$	x
2	5	95	90	500	500	$1 \times 10^{-5}$	0.3	$\Delta$	o
3	10	90	90	500	500	$8 \times 10^{-6}$	0.5	o	o
4	20	80	90	500	500	$8 \times 10^{-6}$	0.9	$\odot$	$\odot$
5	30	70	90	500	500	$8 \times 10^{-6}$	1.5	$\odot$	$\odot$
6	40	60	90	500	500	$1 \times 10^{-5}$	1.5	o	o
7	50	50	90	500	500	$2.5 \times 10^{-5}$	1.5	$\Delta$	o
8	60	40	90	500	500	$7 \times 10^{-5}$	1.5	x	x

(Note)  $\odot$  ... Excellent o ... Good  $\Delta$  ... Fair x ... Poor

## Example 2

Following the same procedure as in Example 1, the conductive paste of sample No. 5 prepared in Example 1 was burnt at various burning temperatures, and resultant characteristics were tested. The test results are shown in Table 2.

Table 2

No.	Glass Content (wt.%)	Copper Oxide Content (wt.%)	Oxidation Ratio (%)	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength (kg/mm <sup>2</sup> )	Soldering Property	Total Evaluation
				In Air	In Hydrogen Atmosphere				
9	30	70	90	300	500	$9 \times 10^{-6}$	1.4	⊙	⊙
10	30	70	90	300	300	$7 \times 10^{-3}$	0.8	○	x
11	30	70	90	400	400	$1.5 \times 10^{-5}$	1.1	⊙	⊙
12	30	70	90	500	300	$3 \times 10^{-3}$	1.1	○	x
13	30	70	90	600	600	$7 \times 10^{-6}$	1.5	⊙	⊙
14	30	70	90	700	300	$1 \times 10^{-2}$	1.0	x	x
15	30	70	90	700	400	$5 \times 10^{-3}$	1.1	x	x
16	30	70	90	700	500	$1 \times 10^{-3}$	1.2	Δ	x

As can be seen from Table 2, when the burning temperature falls within the range of 300°C to 600°C in air and within the range of 400°C to 600°C in a hydrogen atmosphere, the best characteristics can be obtained.

## Example 3

The influence of an oxidation ratio of copper oxide was tested. Conductive pastes and conductors were prepared using compositions and burning temperatures shown in Table 3 following the same procedures as in Example 1, and Table 3 shows the characteristics of the resultant conductors.

Table 3

No.	Glass Content (wt.%)	Copper Oxide Content (wt.%)	Oxidation Ratio (%)	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength ( $\text{kg}/\text{mm}^2$ )	Soldering Property	Total Evaluation
				In Air	In Hydrogen Atmosphere				
17	30	70	1	500	500	$1 \times 10^{-5}$	1.4	⊙	⊙
18	30	70	50	500	500	$8 \times 10^{-6}$	1.5	⊙	⊙
19	30	70	100	500	500	$8 \times 10^{-6}$	1.5	⊙	⊙

As can be seen from Table 3, as the oxidation ratio of copper is increased, better characteristics can be obtained.

## Example 4

The influence of a flattening ratio (a ratio of length/thickness) of the copper oxide powder was tested. Following the same procedures as in Example 1, conductive pastes and conductors were prepared using compositions, types, and burning temperatures shown in Table 4. The characteristics of the resultant conductors are shown in Table 4.

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Table 4

No.	Glass Content (wt.%)	Copper Oxide Content (wt.%)	Flattening Ratio (%)	Oxidation Ratio (%)	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength (kg/mm <sup>2</sup> )	Soldering Property	Total Evaluation
					In Air	In Hydrogen Atmosphere				
20	30	70	1.1	90	500	500	$5 \times 10^{-5}$	1.0	o	o
21	30	70	2	90	500	500	$8 \times 10^{-6}$	1.9	⊙	⊙
22	30	70	8	90	500	500	$7 \times 10^{-6}$	2.1	⊙	⊙
23	30	70	5	95	500	500	$7.5 \times 10^{-6}$	1.7	⊙	⊙
24	30	70	5	10	500	500	$8 \times 10^{-6}$	1.8	⊙	⊙
25	30	70	1.4	99	500	500	$1.5 \times 10^{-5}$	1.1	o	o

(Note) A copper oxide powder having an average particle size of 2  $\mu\text{m}$  was used in sample Nos. 23 to 25.

As can be seen from Table 4, the copper oxide powder having a flattening ratio of 1.5 or higher had better characteristics.

## Example 5

Seventy percent by weight of various copper alloy oxide powders having an average particle size of 1  $\mu\text{m}$  and 30% by weight of  $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$  based glass having a softening point of about  $550^\circ\text{C}$  and a coefficient of thermal expansion of  $7.8 \times 10^{-6}^\circ\text{C}^{-1}$  (glass composition: 11% of  $\text{SiO}_2$ , 81% of  $\text{PbO}$ , 4% of  $\text{B}_2\text{O}_3$ , 3% of  $\text{Al}_2\text{O}_3$ , and 1% of  $\text{ZnO}$ ) were mixed to prepare base materials. The base materials were dispersed in an organic vehicle in which 10% by weight of ethyl cellulose was dissolved in butyl carbitol, thereby preparing conductive pastes. The conductive pastes were screen-printed on alumina boards, and were burnt at predetermined temperatures. The specific resistance, the adhesive strength, and the soldering properties of the resultant conductors were tested. The test results are shown in Table 5.

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Table 5

No.	Alloy Composition	Oxidation Ratio (%)	Burning Temperature (°C)		Specific Resistance ( $\Omega$ -cm)	Adhesive Strength (kg/mm <sup>2</sup> )	Soldering Property	Total Evaluation
			In Air	In Hydrogen Atmosphere				
26	Cu-1%Ag	90	600	500	$8 \times 10^{-6}$	1.5	⊙ +	⊙
27	Cu-10%Ag	90	600	500	$9 \times 10^{-6}$	1.5	⊙ ++	⊙
28	Cu-50%Ag	90	600	500	$1 \times 10^{-5}$	1.5	⊙ ++	⊙
29	Cu-1%Sn	90	600	500	$1 \times 10^{-5}$	1.5	⊙ +	⊙
30	Cu-5%Sn	90	600	500	$2 \times 10^{-5}$	1.5	⊙ ++	⊙

(continued)

No.	Alloy Composition	Oxidation Ratio (%)	Burning Temperature (°C)		Specific Resistance (Ω·cm)	Adhesive Strength (kg/mm <sup>2</sup> )	Soldering Property	Total Evaluation
			In Air	In Hydrogen Atmosphere				
31	Cu-10%Sn	90	600	500	5×10 <sup>-5</sup>	1.5	⊙ ++	○
32	Cu-20%Ag-5%Sn	90	600	500	2×10 <sup>-5</sup>	1.4	⊙ ++	⊙
33	Cu-0.03%Ag	90	600	500	8×10 <sup>-6</sup>	1.5	⊙	⊙
34	Cu-0.005%Sn	90	600	500	8×10 <sup>-6</sup>	1.4	⊙	⊙
35	Cu-60%Ag	90	600	500	2×10 <sup>-6</sup>	1.6	⊙ +	⊙
36	Cu-15%Sn	90	600	500	1×10 <sup>-4</sup>	1.3	⊙	x

(Note) + indicates better and ++ indicates best of the excellent category.

## Example 6

A copper powder having an average particle size of 1  $\mu\text{m}$  and a  $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$  based glass powder (the same composition as in Example 1) were mixed at various mixing ratios to prepare base materials. The base materials were dispersed in an organic vehicle in which 10% by weight of ethyl cellulose was dissolved in butyl carbitol, thereby preparing conductive pastes. The conductive pastes were screen-printed on alumina boards and were burnt at predetermined temperatures. The specific resistance, the adhesive strength, and the soldering properties of the resultant conductors were tested. The test results are shown in Table 6.

Table 6

No.	Glass Content (wt.%)	Copper Content (wt.%)	Burning Temperature ( $^{\circ}\text{C}$ )		Specific Resistance ( $\Omega\cdot\text{cm}$ )	Adhesive Strength ( $\text{kg}/\text{mm}^2$ )	Soldering Property	Total Evaluation
			In Air	In Hydrogen Atmosphere				
37	0	100	500	500	$3 \times 10^{-3}$	0	$\Delta$	x
38	5	95	500	500	$1.1 \times 10^{-5}$	0.3	$\Delta$	o
39	10	90	500	500	$8.5 \times 10^{-6}$	0.5	o	o
40	20	80	500	500	$8.6 \times 10^{-6}$	0.9	$\odot$	$\odot$
41	30	70	500	500	$8.5 \times 10^{-6}$	1.5	$\odot$	$\odot$
42	40	60	500	500	$1 \times 10^{-5}$	1.5	o	o
43	50	50	500	500	$3 \times 10^{-5}$	1.5	$\Delta$	o
44	60	40	500	500	$6 \times 10^{-5}$	1.5	x	x

## Example 7

The conductors were formed on the alumina boards using the conductive paste of sample No. 41 prepared in Example 6 while changing the burning temperature, and the characteristics of the resultant conductors were tested. The test results are shown in Table 7.

Table 7

No.	Glass Content (wt.%)	Copper Content (wt.%)	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength (kg/mm <sup>2</sup> )	Soldering Property	Total Evaluation
			In Air	In Hydrogen Atmosphere				
45	30	70	300	500	$9 \times 10^{-6}$	1.3	⊙	⊙
46	30	70	300	300	$7.3 \times 10^{-3}$	0.8	○	×
47	30	70	400	400	$1.6 \times 10^{-5}$	1.1	⊙	⊙
48	30	70	500	300	$3 \times 10^{-3}$	1.0	○	×
49	30	70	600	600	$3 \times 10^{-6}$	1.5	⊙	⊙
50	30	70	700	300	$2 \times 10^{-2}$	1.0	×	×
51	30	70	700	400	$6 \times 10^{-3}$	1.1	×	×
52	30	70	700	500	$1 \times 10^{-3}$	1.2	Δ	×

As can be seen from Table 7, when the copper powder is used, if the burning temperature falls within the range of 300°C to 600°C in air and within the range of 400°C to 600°C in a hydrogen atmosphere, conductors having good characteristics can be obtained.

## Example 8

The influence of a flattening ratio (a ratio of length/thickness) of the copper powder on the characteristics of the conductor was tested. Following the same procedures as in Example 6, conductive pastes and conductors were prepared using compositions, types, and burning temperatures shown in Table 8. The characteristics of the resultant conductors are shown in Table 8.

Table 8

No.	Glass Content (wt.%)	Copper Content (wt.%)	Flat-tening Ratio (%)	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength ( $\text{kg/mm}^2$ )	Solder- ing Pro- perty	Total Evalua- tion
				In Air	In Hydrogen Atmos- phere				
53	30	70	1.1	500	500	$5 \times 10^{-5}$	1.0	○	○
54	30	70	1.4	500	500	$1.5 \times 10^{-5}$	1.1	○	○
55	30	70	2	500	500	$8 \times 10^{-6}$	1.9	⊙	⊙
56	30	70	5	500	500	$8 \times 10^{-6}$	1.7	⊙	⊙
57	30	70	5	500	500	$9 \times 10^{-6}$	1.8	⊙	⊙
58	30	70	8	500	500	$7.5 \times 10^{-6}$	2.1	⊙	⊙

As can be seen from Table 8, the copper powder having a flattening ratio of 1.5 or more can provide good characteristics.

#### 5 Example 9

Seventy percent by weight of copper alloy powders having compositions shown in Table 9 and an average particle size  $1\ \mu\text{m}$  and 30% by weight of a  $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$  based glass powder having a softening point of about  $350^\circ\text{C}$  and a coefficient of thermal expansion of  $11 \times 10^{-6}^\circ\text{C}^{-1}$  (glass composition: 4% of  $\text{SiO}_2$ , 85% of  $\text{PbO}$ , 18% of  $\text{B}_2\text{O}_3$ , 1% of  $\text{Al}_2\text{O}_3$ , and 2% of  $\text{ZnO}$ ) were mixed to prepare base materials. The base materials were dispersed in an organic vehicle in which 10% by weight of ethyl cellulose was dissolved in butyl carbitol, thereby preparing conductive pastes. The conductive pastes were screen-printed on alumina boards, and were burnt at temperatures shown in Table 9. The specific resistance, the adhesive strength, and the soldering properties of the resultant conductors were tested. The test results are shown in Table 9.

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Table 9

No.	Alloy Composition	Burning Temperature (°C)		Specific Resistance ( $\Omega \cdot \text{cm}$ )	Adhesive Strength ( $\text{kg/mm}^2$ )	Soldering Property	Total Evaluation
		In Air	In Hydrogen Atmosphere				
59	Cu-1%Ag	500	500	$8 \times 10^{-6}$	1.5	⊙ +	⊙
60	Cu-10%Ag	500	500	$9 \times 10^{-6}$	1.5	⊙ ++	⊙
61	Cu-50%Ag	500	500	$1 \times 10^{-5}$	1.5	⊙ ++	⊙
62	Cu-1%Sn	500	500	$2 \times 10^{-5}$	1.5	⊙ +	⊙
63	Cu-5%Sn	500	500	$5 \times 10^{-5}$	1.5	⊙ ++	○
64	Cu-10%Sn	500	500	$7 \times 10^{-5}$	1.5	⊙ ++	Δ

(continued)

No.	Alloy Composition	Burning Temperature (°C)		Specific Resistance (Ω·cm)	Adhesive Strength (kg/mm <sup>2</sup> )	Soldering Property	Total Evaluation
		In Air	In Hydrogen Atmosphere				
65	Cu-20%Ag-5%Sn	500	500	$2 \times 10^{-5}$	1.4	⊙ ++	⊙
66	Cu-0.03%Ag	500	500	$8 \times 10^{-6}$	1.5	⊙	⊙
67	Cu-0.005%Sn	500	500	$8 \times 10^{-6}$	1.4	⊙	⊙
68	Cu-60%Ag	500	500	$2 \times 10^{-6}$	1.6	⊙ +	⊙
69	Cu-15%Sn	500	500	$1 \times 10^{-4}$	1.3	⊙	x

(Note) + indicates better and ++ indicates best of the excellent category.

#### Claims

1. A low-temperature burnt conductive paste characterized in that a base material comprising 50 to 95% by weight of a powder of at least one conductive material selected from the group consisting of copper, a copper alloy containing copper as a major component, and oxides thereof and 5 to 50% by weight of a glass powder having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $6$  to  $13 \times 10^{-6}/^{\circ}\text{C}$  is dispersed in an organic vehicle.
2. A paste according to claim 1, characterized in that the average particle size of said conductive material powder is not more than  $10 \mu$ .

3. A paste according to claim 1, characterized in that said conductive material powder comprises an oxide powder of copper or a copper alloy having an oxidation ratio of 0.1 to 100%.

4. A paste according to claim 1, characterized in that said conductive material powder is a copper powder.

5. A paste according to claim 1, characterized in that said conductive material is flattened to have a flattening ratio (a ratio of length/thickness) of at least 1.5.

6. A paste according to claim 1, characterized in that the copper alloy is an alloy selected from the group consisting of Cu-Ag, Cu-Sn, and Cu-Ag-Sn, an Ag content falling within the range of 0.05 to 50% by weight, and an Sn content falling within the range of 0.01 to 10% by weight.

7. A paste according to claim 1, characterized in that said glass powder having the softening point of 300 to 600°C and the coefficient of thermal expansion of  $8$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  is lead-borosilicate glass containing  $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$  as a major component.

8. A method of manufacturing a printed circuit board characterized in that a circuit pattern is formed on an electrical insulating inorganic board by a desired process using a burnt conductive paste prepared by dispersing, in an organic vehicle, a base material comprising 50 to 95% by weight of a powder of at least one conductive material selected from the group consisting of copper, a copper alloy containing copper as a major component, and oxides thereof and 5 to 50% by weight of a glass powder having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $8$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  and the resultant structure is heated in air at a temperature of 300 to 600°C and is subsequently heated in a reducing atmosphere at a temperature of 400 to 600°C.

9. A method according to claim 8, characterized in that said electrical insulating inorganic board is a board selected from the group consisting of a ceramic board and a porcelain enamel board.

10. A method according to claim 8, characterized in that said burnt conductive paste is screen-printed to form said circuit pattern.

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# EUROPEAN PATENT APPLICATION

21 Application number: 87106482.0

51 Int. Cl.5: H05K 1/09

22 Date of filing: 05.05.87

30 Priority: 27.08.86 JP 200731/86

43 Date of publication of application:  
02.03.88 Bulletin 88/09

84 Designated Contracting States:  
DE FR GB IT NL

88 Date of deferred publication of the search report:  
14.03.90 Bulletin 90/11

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54 Low-temperature burnt conductive paste and method of manufacturing printed circuit board.

57 Disclosed are a low-temperature burnt conductive paste which is prepared in such a manner that a base material consisting of 50 to 95% by weight of a powder of at least one conductive material selected from the group consisting of copper, a copper alloy containing copper as a major component, and oxides thereof and 5 to 50% by weight of a glass powder having a softening point of 300 to 600°C and a coefficient of thermal expansion of  $6$  to  $13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  is dispersed in an organic vehicle, and a method of manufacturing a printed circuit board using the paste.

EP 0 257 193 A3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 87 10 6482

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 125 730 (CENTRALAB INC.) * claims 1,2,9-11; abstract *	1-4,6-9	H 05 K 3/12 H 01 B 1/16 H 05 K 1/09
X	EP-A-0 131 778 (DU PONT DE NEMOURS AND COMPANY) * claims 1-12 *	1-4,6-9	
A	EP-A-0 135 174 (DU PONT DE NEMOURS AND COMPANY) * claims 1-4,8 *	1,2,4,6,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			H 05 K 3/00 H 01 B 1/00 H 05 K 1/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 27-11-1989	Examiner HAHN G
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			